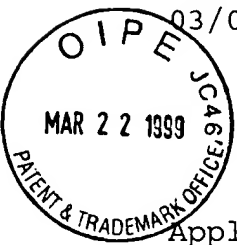


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PATENT APPLICATION
Attorney's Docket No.: TEX98-01A



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

8 1/2

Applicant: David M. Mayes
Application No.: 09/019,667 Group: 2877
Filed: 06 February 1998 Examiner: Nguyen, T.
For: GRAIN QUALITY MONITOR

DECLARATION OF DAVID M. MAYES

Sir:

1. My name is David M. Mayes.
2. I presently reside at 807 Penn Avenue, LaGrande, Oregon 97850.
3. I am the inventor in the above-referenced patent application.
4. I hold a doctorate degree in Chemistry from the University of Washington, in Seattle, Washington.
5. I am generally familiar with the applications of near-infrared (NIR) spectroscopy to process analysis, having been one of the authors of a paper entitled "NIR applications in process analysis", American Laboratory, October 1989, pp. 54-58. A copy of my paper is attached as Appendix A.
6. That paper describes a number of applications of NIR spectroscopy in the grain and food industry, including the laboratory and on-line analysis of the protein, moisture, texture, and hardness of wheat and other grain products; fat content in meat and dairy products; analysis of cotton and wool;



and a "host of other foodstuffs". [See the third paragraph in the left hand column of page 57 of the paper in Appendix A.]

7. In approximately 1992, I was first involved with a project that related to the development of a a new type of NIR spectrometer.

8. As a result of that project, an improved compact NIR spectrometer was developed that was based on the use of charge coupled device (CCD) arrays. This spectrometer, called the "DPA200 Spectrophotometer System", was described in a paper I authored entitled "A compact, solid state spectrophotometer system for process monitoring", Process Control and Quality, Vol. 5 (1993), pp. 1-8 (Appendix B).

9. That paper details the difficulties with the then-existing NIR instruments which relied upon scanning gratings and discrete filters. As we mentioned in that paper, scanning devices tend to drift in terms of wavelength accuracy due to mechanical wear making frequent recalibration necessary, and filter devices are limited in the amount of spectral information they provide.

10. As described in the paper attached as Appendix B, the DPA200 spectrophotometer incorporated a 1024 element CCD detector array for acquiring spectral information and a proprietary passive wavelength dispersion device [first paragraph, right hand column, page 3]. The proprietary device referred to here was a type of linear variable filter (LVF) which provided dispersion over the

desired infrared wavelengths.

11. A stabilized tungsten/halogen lamp supply provided a light source; and the detector used a single 600 um optical fiber for spectral data acquisition. [last paragraph, left hand column, page 3].

12. The CCD detector offers the unique feature of obtaining a full spectrum in one time period, unlike other electronic scanning devices such as photo diode arrays in which the individual diodes must be scanned over time, and unlike filter or scanning grating devices in which the wavelengths are scanned over time.

13. Later versions of this spectrophotometer also incorporated a grin lens attached to the output of the optical fiber. The grin lens was used ^{as a} mode mixer.

14. The DPA spectrophotometer system described above was sold before December 1995.

16. To my knowledge, the DPA spectrophotometer was used or suggested for use in a number of applications, including the determination of the hematocrit of blood, visible fiber optic sensors, flow injection analysis, differentiation of ABS and HIPS plastics for recycling, determination of fat content in fish.

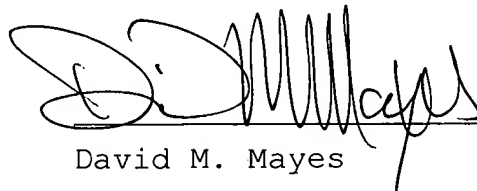
17. However, prior to December 1995, the above described DPA

spectrophotometer systems were not used for analyzing the properties of grain.

18. In addition, prior to December 1995, the DPA spectrophotometer systems were not used or mounted to mobile agricultural equipment such as a combine or harvester.

19. Furthermore, prior to December 1995, the DPA systems were not used to determine the properties of grain as it is being harvested in the field.

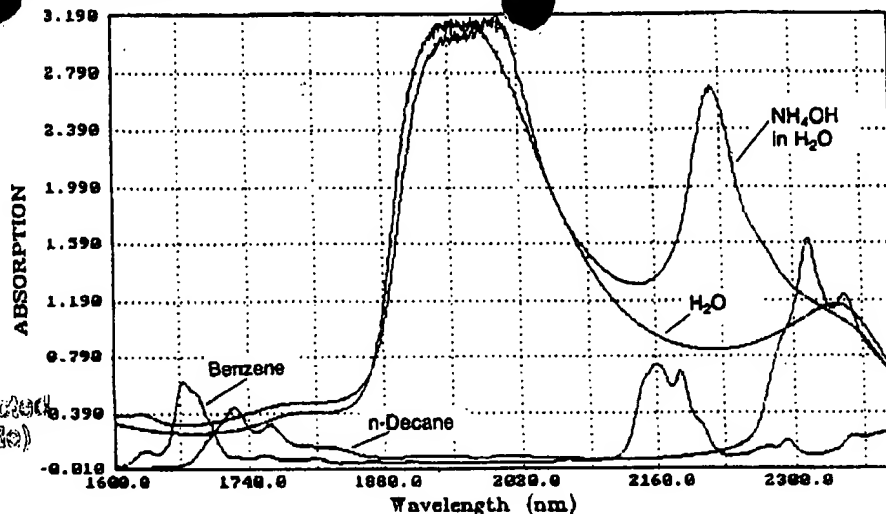
20. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under \$1001 of Title 18 of the United States Code, and that such willful, false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this Declaration is directed.



David M. Mayes

3-8-99

(Date)



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NIR applications in process analysis

NEAR INFRARED (NIR) spectroscopy brings unique analytical capabilities to process analytical chemistry and industrial process monitoring. It promises more accurate control of industrial processes, reduced processing times, and reduced waste.¹⁻⁴

Traditionally, plant operators have relied upon measurements of temperature, pressure, and flow rate to determine the status of a system. Unfortunately, these measurements relate only directly to the accomplishment of process objectives because many control algorithms require that chemical composition be known. While NIR offers significant capability for determining composition, practical instrumentation for monitoring such processes must be reliable, fast, and enable easy data collection. In the last few years, NIR has been finding its way from the laboratory to the process environment with some success. The merits of NIR analysis, especially those pertinent to process monitoring, will be discussed.

Near infrared spectroscopy, as defined by the ASTM (American Society for Testing and Materials) Working Group, encompasses the range of the electromagnetic spectrum from 780 nm to 2526 nm. In the late 1950s and early 1960s, Karl Norris and co-workers at the Instrumentation Research Laboratory at the USDA Agricultural Marketing Services (Beltsville, Maryland) began to develop instrumental and multilinear regression methods for determining properties of agricultural samples such as wheat and soy beans with NIR spectroscopy. This inspired others to start investigating additional applications for NIR. However, the broad overlapping bands indigenous to spectra in this region make

spectral interpretation very difficult. Nonetheless, NIR has been the topic of several excellent review and application articles since the time Norris began his work.⁵⁻⁸

Central to the use of NIR data are the computer algorithms which reduce the complex spectra to usable information. Only now, with personal computers and advanced data analysis techniques becoming common in the laboratory is NIR finally finding its place in analytical chemistry.

NIR is often divided into two different spectral regions—the shortwave NIR (SW-NIR), 700 nm to 1100 nm, and the traditional NIR, from 1100 nm to 2500 nm—based on the different types of detectors used. Silicon, which becomes increasingly transparent to light above 1100 nm, is used for the SW-NIR region because of its high signal-to-noise (S/N) characteristics, large dynamic range, and low cost. Lead sulfide (PbS), germanium (Ge), and indium/gallium/arsenide (InGaAs) are the most common detector materials for the longer wavelength region.

Spectroscopy in both regions of the NIR deals with overtones and combinations of fundamental absorptions occurring in the mid-IR region of C-H, O-H, and N-H functional groups. In addition, electronic transitions of highly conjugated compounds appear in the SW-NIR. Because the X-H absorbancies are those of overtone and combination bands, their molar absorptivities are quite small and the resulting absorbance spectra are highly overlapped. Since the molar absorptivities are small, pathlengths for undiluted liquid samples can be up to a centimeter in the NIR and from 0.5 cm to over 10 cm in the SW-NIR, depending on the type of sample. Figures 1a, b, and c illustrate some common spectral features found in the NIR. Spectra of water, ammonium hydroxide in water, n-decane, and benzene, replicated in three different areas of the NIR spectral region—700-1100 nm, 1100-1600 nm, and 1600-2400 nm—present

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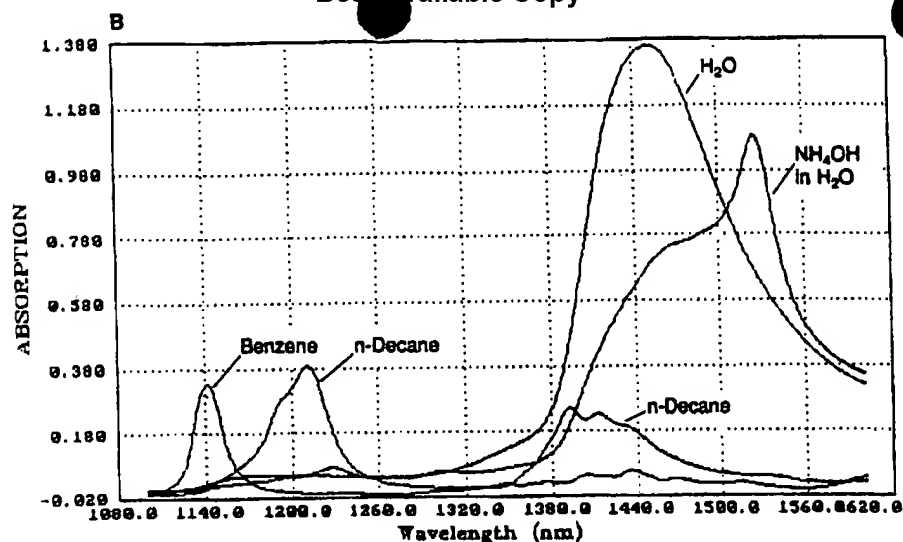
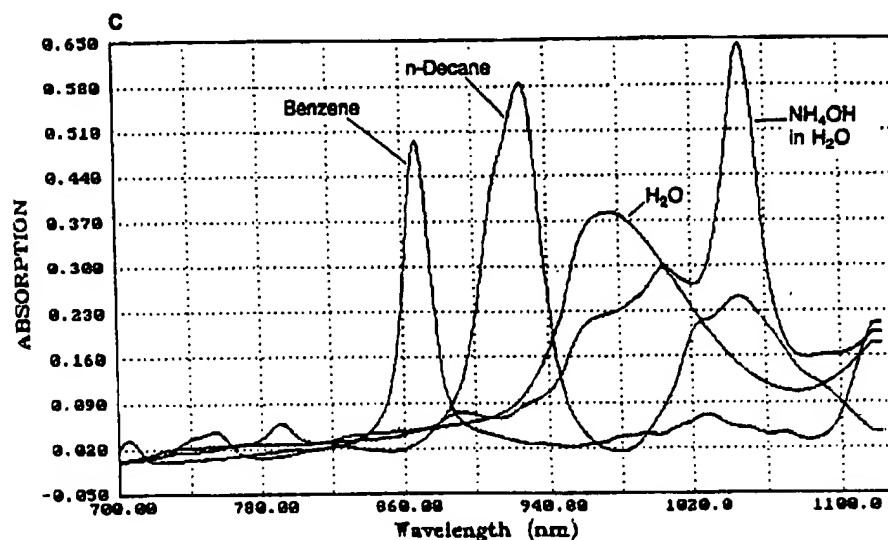


Figure 1 Common spectral features found in the NIR.



similar functional group information though longer pathlengths in the shorter wavelength ranges. In Figures 1a and b, a 1.0-mm cuvette was used for water and the ammonium hydroxide solution, and in Figure 1c, a 20-mm cuvette was used. While the pathlengths used in Figures 1a and b are the same, the optical densities of the absorption bands are much greater in the region between 1600 and 2400 nm than in the 1100-1600 nm region. Indeed, the water and ammonium hydroxide bands are over-absorbed in the 1960-nm region. The 700-1100 nm region reveals the same basic information through a much greater pathlength. For benzene and n-decane, a 1-mm cuvette was used in the 1600-2400 nm region, a 5-mm cuvette in the 1100-1600 nm region, and a 10-cm cuvette in the 700-1100 nm region. Note that in all the spectra, aromatic C-H bands are clearly separated from those of aliphatic C-H, and that one can distinguish between methyl and methylene groups in decane.

The relatively long pathlengths permitted in the NIR eliminate the thin film sampling problems inherent in mid-IR spectroscopy and present data more representative of the bulk media. Weak molar absorptivities, however, usually limit typical NIR analyses to the detection of constituents greater than 0.1%-1.0% by weight. For

the detection of water in hydrocarbons or the reverse, 100-ppm and higher levels can be accurately determined because the absorption bands of water and of hydrocarbons are clearly separated. For other analyses in which the spectral features are quite overlapped, sophisticated data analysis techniques such as Multilinear Regression (MLR), Principal Components Regression (PCR), and Partial Least Squares (PLS)⁹ must be used to obtain meaningful correlations.

Instrumentation

While many NIR instruments can be configured to collect data from the UV through the NIR, most excel in the 1100-2400 nm region. They all have scanning grating monochromators with a PbS or Ge detector for the NIR region. Sampling configurations include transmission, diffuse reflectance, and reflectance, which enable the instruments to analyze all types of samples from solids and slurries to liquids and even gases, as well as fiber optic capabilities for remote sensing. Some manufacturers also produce an instrument designed for use in a process environment. However, the scanning grating common to all of these instruments is subject to instrumental drift and failure with extended long-term

use. In recent work by Mayes and Callis,¹⁰ instrumentation based on photodiode array technology with a fixed grating for the SW-NIR region eliminated the need for mechanical components, thus creating a more rugged design.

Applications

For process monitoring, what advantages does NIR have over other spectroscopic methods? Although temperature extremes, vibrations and shocks, corrosive atmospheres, and placement locations limited by potential hazards constitute major obstacles in the design of a field instrument, sampling presents the biggest dilemma. In many instances it can make or break a specific technique. Because NIR can be used with fiber optics to isolate the instrument from the process stream and harsh environments, many of the design problems can be obviated. Thus, sample probes can be designed for direct placement in a process stream or to be completely noninvasive to a process stream.^{11,12} This not only eliminates sample handling, but provides a means in which to monitor a system without fear of contamination or perturbation of the system in the course of removing a sample for analysis, a very attractive feature. Other characteristics, such as long pathlengths and the ability to look at a wide variety of sample conditions, alleviate many of the other problems associated with obtaining a sample to measure. In addition, NIR is fast; in most cases, a sample can be analyzed and an answer obtained in less than one minute.

Current laboratory and on-line¹³ NIR applications include the analysis of the protein, moisture, texture, and hardness of wheat and other grain products;^{14,15} fat content in meat and dairy products;^{16,17} analysis of cotton and wool;^{18,19} and a host of other foodstuffs.²⁰ Some researchers have also found NIR to be a useful tool in the analysis of other biological systems, such as percent oxygenation of hemoglobin,²¹ noninvasive analysis of body fat,²² and determination of serum cholesterol.²³ Surely if NIR is capable of analyzing samples as complicated as plant matter and the human body, it should be feasible to use it in the area of process monitoring.

The strong absorbance of H₂O in several regions of the NIR and the critical need for moisture determination in many processes account for the extensive use of NIR in such applications as moisture analysis in dryers, organic solvents, and alcohols.²⁴ A recently reported technique described for the use of NIR to determine NaOH concentration in caustic and caustic brines in the 0-10% range.²⁵ It noted that the NIR spectrum of water is very sensitive to temperature and ion content of the solution.

In the pharmaceutical industry, NIR has been used as an identifier of active components²⁶ and in the determination of enantiomeric purity.²⁷ Here, NIR, used as

a screening tool, quickly evaluated the bulk properties of a sample and identified sample with reasonable precision.

Polymer analysis has received the most attention with reports of its use as far back as the late 1940s. While early accounts were directed toward band assignments and polymer structure,²⁸ it was soon realized that NIR had the ability to yield results such as plastic composition²⁹ and average molecular weight.³⁰ Other reports have shown NIR useful in polymer identification.³¹ Buback has shown that it is possible to monitor polymerization of pure ethylene at high pressures.³² Here, pure ethylene was placed in a special reaction vessel with optical windows such that spectra could be obtained throughout the time course of the polymerization. This work could easily be extended in developmental studies of catalyst activities and pressure and temperature effects on a given polymerization reaction. Most interesting, however, is the realization that NIR can determine properties of polymers such as tensile strength, elongation, haze, and other engineering grade specifications. Ghosh and Rodgers³³ show that the determination of heatset, a measure of crystallinity, in Nylon 6 and 66 yarns is possible. Because these engineering properties are actually a function of chemical composition (i.e., the amount of polymerization, the amount of branching, etc.), it is reasonable that NIR can correlate these chemical properties with those of the engineering world. Currently, the determination of most engineering specifications requires substantial time and the destruction of the sample. With NIR, it is possible to measure these properties in almost real time and in the process stream, thus allowing better control of the process.

The analysis of hydrocarbon substances, mixtures, and composites is currently an area of intense research. In 1956, Holman and Edmondson³⁴ showed that NIR can analyze different types of fatty acids and related substances. While no chemometric techniques were used, many characteristic bands could be assigned to different functional groups, including the ability to distinguish between cis and trans conformations. Following these results, others determined unsaturation using the ratio of the methyl and methylene bands,³⁵ functional groups in epoxy resins,³⁶ and structural group analysis of hydrocarbon mixtures.³⁷ While these papers illustrate the ability of NIR to distinguish between functional groups, only recently have investigators combined chemometric techniques and NIR and discovered the wide applicability of these methods. As in the analysis of polymers, NIR has the potential of correlating many properties of substances with their spectral features. Honigs et al.³⁸ determined heats of formation, number of methyl groups per molecule, and molecular weight (as a means to measure viscosity). Donahue et al.³⁹ assessed the BTU content of natural gas mixtures

(methane, ethane, and propane) at pressures from 100 to 1000 psi with an average error of less than 0.5%. Callis et al.⁴⁰ reported the simultaneous determination of research and motor octane, Reid vapor pressure, API gravity, and several other parameters of gasoline and blending stocks. From these few examples, one can anticipate that many other properties have the potential of being monitored by NIR. As quoted from Honigs et al.,³⁸ "With all of the physical-property information available in the near-infrared spectrum of a sample, it is reasonable to wonder what physical properties cannot be determined by near-infrared analysis." One need only determine that a parameter of interest correlate with some characteristic chemical functionality that absorbs in the NIR region.

Despite the obvious need for rapid analysis of these types of control parameters in modern high volume chemical plants, few application notes have been published, apparently discouraged by industry.⁸ Although this has greatly limited the growth of NIR analysis, those that have appeared clearly indicate much potential for NIR. One article⁴¹ describes NIR applications in a variety of process areas resulting in decreased turnaround time for analysis and rapid payback of the instrumentation costs. Another paper¹¹ describes similar results, and another compares the results obtained using two different analyzers for beer analysis.⁴² These papers describe NIR in numerous process control applications from monitoring adhesive thickness and resin content in a solvent mixture to control of feed rates in continuous flow and endpoint detection for batch processes.

The apt title of a short review of NIR,⁴³ "Near infrared spectroscopy: Time for the giant to wake up," suggests the substantial potential for NIR in process analytical chemistry. It includes raw material analysis for analyzing feed stocks, reactor monitoring, final product testing, and waste evaluation, among others. One need only think of an application and try it, and it just might work.

References

- HIRSCHFELD, T., CALLIS, J.B., and KOWALSKI, B.R., *Science* 226, 312 (1984).
- CALLIS, J.B., ILLMAN, D.L., and KOWALSKI, B.R., *Anal. Chem.* 59 (9), 624A (1987).
- JACOBS, S.M. and MEHTA, S.M., *Am. Lab.* 19 (12), 15-22 (1987).
- HONIGS, D.E., *Am. Lab.* 19 (12), 48-51 (1987).
- KAYE, W., *Spectrochimica Acta* 6, 257 (1954).
- WHETSEL, K.B., *Appl. Spectrosc. Rev.* 2 (1), 1 (1968).
- WEYER, L.G., *Appl. Spectrosc. Rev.* 21 (1), (1985).
- STARK, E. and LUCHTER, K., *Appl. Spectrosc. Rev.* 22 (1), 335 (1986).
- SHARAF, M.A., ILLMAN, D.L., and KOWALSKI, B.R., *Chemometrics* (John Wiley & Sons, New York, NY, 1986).
- MAYES, D.M. and CALLIS, J.B., *Appl. Spectrosc.* 43 (1), 27 (1989).
- FITCH, P. and GARGUS, A.G., *Am. Lab.* 17 (12), 64-71 (1985).
- WEYER, L.G., BECKER, K.J., and LEACH, H.B., *Appl. Spectrosc.* 41 (1), 786 (1987).
- MC DONALD, N. and STREANER, R., *Australasian Baking*, May/June, 19ff (1987).
- OSBOURNE, B.G., *Anal. Proc.* 20, 70 (1983).
- OSBOURNE, B.G. and FEARN, T., *J. Sci. Food Agric.* 34, 1011 (1983).
- GELADI, P., MAC DOUGALL, D., and MARTENS, H., *Appl. Spectrosc.* 39 (3), 491 (1985).
- ROBERT, P., BERTRAND, D., and DEVAUX, M.F., *Anal. Chem.* 59, 2187 (1987).
- GHOSH, S., *Proceedings of the 7th International Symposium on Near-Infrared Reflectance Analysis (NIRA)* (Technicon Industrial Systems, Tarrytown, New York, 1984).
- CONNELL, J.P. and BROWN, G.H., *J. Text. Inst.* 69 (12), 357 (1978).
- HIRSCHFELD, T. and STARK, E.W., *Analysis of Foods and Beverages* (Academic Press Inc., New York, NY, 1984).
- JOBSIS, F.F., *Science* 198, 1264 (1977).
- CONWAY, J.M., NORRIS, K.H., and BODWELL, C.E., *Am. J. Clin. Nutr.* 40, 1123 (1984).
- PEUCHANT, E., SALLES, C., and JENSEN, J., *Anal. Chem.* 59, 1816 (1987).
- WEYER, L.G., BECKER, K.J., and LEACH, H.B., *Appl. Spectrosc.* 41 (5), 786 (1987).
- BAUGHMAN, E.H. and WATSON, E., JR., *Spectrosc.* 2 (1), (1987).
- CIURCZAK, E.W. and MALDACKER, T.A., *Spectrosc.* 1 (1), 36 (1986).
- BUCHANAN, B.R. et al., *Spectrosc.* 3 (5), 54 (1988).
- GLATT, L. and ELLIS, J.W., *J. Chem. Phys.* 19 (4), 449 (1951).
- WEYER, L.G., *J. Appl. Poly. Sci.* 31, 2417 (1986).
- LE FEVRE, R.J.W., PARKINS, G.M., and ROPER, R., *Aust. J. Chem.* 13, 169 (1960).
- DAVIES, A.M.C. et al., *Analyst* 110, 643 (1985).
- BUBACK, M. and LENDLE, H., *Makromol. Chem.* 184, 193 (1983).
- GHOSH, S. and RODGERS, J.E., *Text Res. Inst.* 556 (1985).
- HOLMAN, R.T. and EDMONDSON, P.R., *Anal. Chem.* 28 (10), 1533 (1956).
- GODDU, R.F., *Anal. Chem.* 29 (12), 1790 (1957).
- DANNENBERG, H., *SPE Trans.* 1, 78 (1963).
- BERNHARD, U. and BERTHOLK, P.H., *Jena. Rev.* 20 (5), 248 (1975).
- HONIGS, D.E., HIRSCHFELD, T., and HIEFTJE, G.M., *Anal. Chem.* 57 (2), 443 (1985).
- DONAHUE, S.M. et al., *Anal. Chem.* 60 (18), 1873 (1988).
- KELLY, J.J. et al., *Anal. Chem.* 61 (4), 313 (1989).
- MACZKA, W.J., *Iniech* 35 (11), 30 (1988).
- REEVE, P. and WHITE, H., *Food Science Technology Today*, June, 131ff (1988).
- DAVIES, A.M.C., *European Spectroscopy News* #73, 10ff (1987).

Application

A compact, solid state spectrophotometer system for process monitoring *

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Abstract

Near-infrared spectroscopy has become an acceptable means for process monitoring in many industrial settings besides the agricultural/food industry. With its growing acceptance, the need for improved spectrophotometers that have been designed for the process environment and exhibit long term stability is crucial to the successful implementation of this technology. A compact charged coupled device (CCD) array based spectrophotometer is discussed that has been designed specifically for the industrial setting. Its design features are outlined and performance is summarized in terms of signal-to-noise ratio, dynamic range, spectral resolution, long term stability, and potential benefits over existing commercially available instruments.

Keywords: Near-infrared spectroscopy; Charge coupled device array; Process monitoring

1. INTRODUCTION

In the past decade, near-infrared (NIR) spectroscopy from 700–2500 nm has enjoyed a rather large increase in popularity as an analysis technique for many types of materials. Because it can easily analyze liquid, slurry, and solid samples without special preparation, it is especially useful as an on-line measurement technique in industrial set-

tings. It has been reported in the literature as a tool to measure constituent information of samples from the petrochemical, pharmaceutical, agriculture/food, plastics, medical, textile, and biotechnology industries [1,2]. Unfortunately, many of the NIR instruments currently available rely on scanning gratings or discrete filters in their designs and thus pose limitations when considered for use as a process monitor. Scanning grating instruments tend to drift in terms of wavelength accuracy due to mechanical wear making recalibration a necessity at frequent intervals. Filter based instruments usually do not drift in wavelength accuracy but are inherently

* Presented at FACSS XIX, Philadelphia, P.A. September 20–25, 1992.

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limited in the amount of spectral information which is set by the small number of band pass filters incorporated in their design.

Recently, several spectrophotometers for the short wavelength near-infrared region (SW-NIR: 700–1100 nm) have been discussed in the literature that are based on linear photo diode array technology and a fixed grating spectrograph [3,4]. The reported advantages are obvious considering that 1024 channels of wavelength information are obtained simultaneously with no moving parts. Furthermore, the SW-NIR region is quite appealing for process monitoring due to the relatively small absorptivity coefficients of different substances in this region allowing sample path lengths to be between 1 mm and 100 mm. This unique feature makes a monitoring system more immune to fouling by thin layers of matter that may accumulate on a flow-through cell window. In addition, it provides more robust information in terms of analyzing bulk constituents.

In this paper, the DPA200 spectrophotometer system is described which has been designed specifically for the process environ-

ment. Its design was governed by the idea to produce a small, inexpensive, rugged spectrophotometric analyzer that could operate without the need of a host computer. It embodies a solid state silicon photo detector array, miniaturized optical components, an embedded 32-bit RISC computer processor, and a means to directly communicate to external devices. The remainder of this paper discusses the instrument and its performance specifications.

2. INSTRUMENT DISCUSSION

The DPA200 spectrophotometer was designed to be as flexible as possible to accommodate many different applications and was therefore modularized into three basic sub-assemblies: 32-bit RISC computer processor, power/environmental system, and detector and analog to digital circuits (Fig. 1). This flexibility permits new technologies to be easily integrated into an existing system such as an InGaAs detector array for spectral acquisition in the 900–1800 nm region. The entire system is packaged in a $12 \times 16 \times 30$ cm

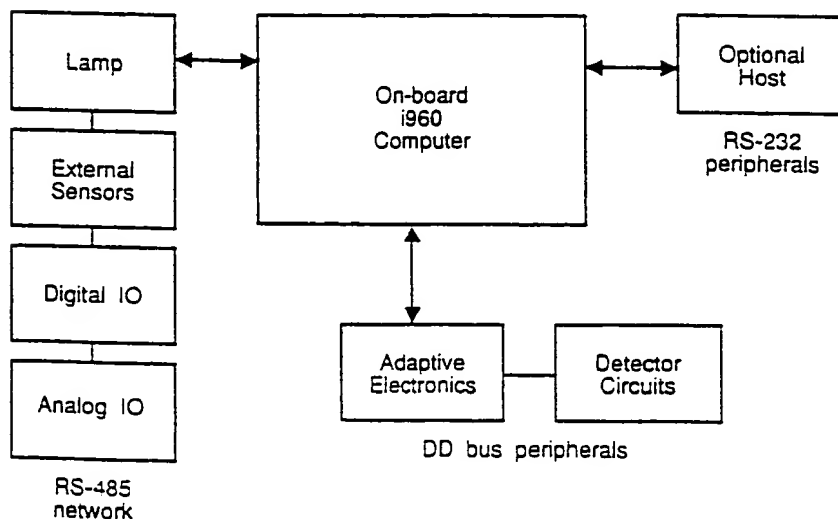


Fig. 1. Block diagram of instrument.

NEMA 2 enclosure and can easily be sealed for NEMA 4, 4X, and 12 ratings or repackaged for NEC Class 1 Division 1 explosion proof installations. For added versatility, the on-board computer can communicate with up to 128 different peripherals via a RS-485 network on industrial standard I/O components. This allows the spectrophotometer to easily control devices such as valves, pumps, motion controllers, etc., and accept information from external sensors such as triggering devices, temperature, pressure, and flow.

2.1. RISC Computer processor

Integral in the design is a powerful 32 bit RISC computer based on an Intel 80960 (1960) processor. This processor is equal to most desktop i486 PC computers in terms of processing power and runs a specialized operating system that has been designed specifically to perform real-time chemometric spectral analysis, outlier detection, extensive diagnostics, and monitor/control of external devices. An embedded computer processor is essential for an industrial instrument design because it eliminates the need of a host computer to perform routine analyses. The design also incorporates a 'watch dog timer' to automatically reset the instrument in the unlikely event of a system crash.

2.2. Environmental / power system

The DPA200 has a separate environmental and power system that incorporates a separate micro controller. This sub-system controls the thermal electric cooler for the detector array and monitors the instrument's internal temperature. The i960 processor controls this sub-system via an optically isolated communication link. A similar sub-system controls the stabilized tungsten/halogen lamp supply and monitors lamp current and output intensity.

2.3. Detector and analog / digital assemblies

The detector sub-system can be configured for either the visible (400-700 nm) or short wavelength near-infrared (SW-NIR: 700-1100 nm) regions. Both configurations incorporate a 1024 element Charged Coupled Device (CCD) detector array for acquiring spectral information, a 16-bit A/D converter, and a proprietary passive wavelength dispersion device that occupies a mere 8 cm³. The entire detector assembly measures 9 × 4.5 × 2.5 cm and is temperature stabilized to 0 ± 0.1°C with a solid state thermal electric cooler for decreased dark charge signal during slow scan speeds and for long term stability. A CCD detector offers the unique feature of obtaining a full spectrum in one time period unlike other electronic scanning devices such as photo diode arrays in which the individual diodes are scanned over time and acousto-optical tunable filter (AOTF), scanning grating, and filter based instruments where the wavelengths are scanned over time. This feature is important when studying time dependent spectra in reactions or other evolving systems.

The detector module accepts a single 600 μm optical fiber for spectral data acquisition. Each detector module incorporates an electronic ID which can be interrogated by the RISC processor to determine the exact wavelength region and any calibration constants such as wavelength and detector photon efficiency information. This information is used to properly conform the A/D circuits and computer algorithms to the particular module in case it is changed by the user. The scan rate of the detector can be manually or automatically adjusted from 25 ms/scan to over 1 min/scan in 1.0 millisecond intervals. This functionality allows the instrument to adjust the amount of light collected by the CCD detector before readout to fully opti-

mize the detector and A/D converter signal to noise ratio. This method of optimizing signal to noise is superior to other designs that maintain a constant scan speed and merely incorporate a programmable gain stage that amplifies both the photon signal and detector noise equally. Other features of the A/D circuit include computer controlled fine tuning of the detector gain and offset. Because there can be substantial differences between two CCD detector chips in terms of dark charge current and photon conversion efficiency, the DPA200 was designed with the ability to adjust the dark charge (zero light intensity) value of the A/D and the detector signal gain slope. This ensures that each instrument converts a specific photon intensity to the same digital signal thus reducing instrument to instrument variations. It should be realized that the adjustment of these parameters are only performed when the instrument is initialized or upon request of the user.

Of particular importance is the instrument performance specifications in terms of signal-to-noise, dynamic range, spectral resolution, and long term stability. The following is a discussion of these characteristics.

2.3.1. Signal-to-noise

Spectra of light throughput in the visible and SW-NIR regions are illustrated in Fig. 2 and show the light intensity reaching the detector with no sample in the optical path. The shape of the spectral intensity is a function of optical throughput, detector sensitivity, and lamp intensity. If two of these spectra are acquired, the baseline noise at zero absorbance can be calculated by the following equation:

$$A_z = \log_{10} \left(\frac{I_r - D}{I - D} \right) \quad (1)$$

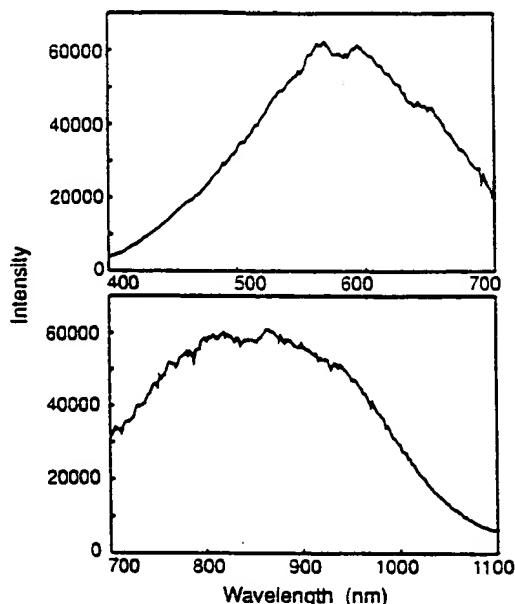


Fig. 2. Intensity spectra of light throughput in the visible and SW-NIR spectral regions.

where A_z is the zero absorbance, I_r is the reference zero absorbance spectrum and I is a subsequent zero absorbance spectrum, and

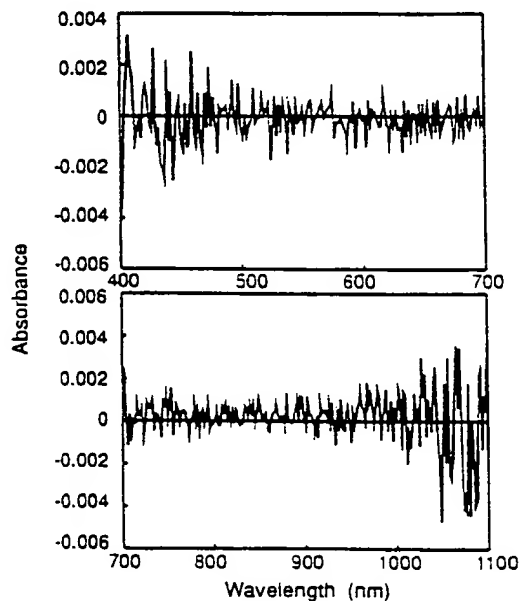


Fig. 3. Baseline noise spectra for 1 scan (25 ms scan rate) in the visible and SW-NIR spectral regions.

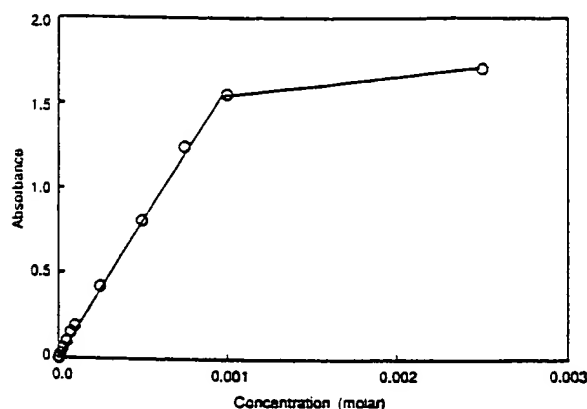


Fig. 4. Stray light study of absorbance vs. molar KMnO_4 concentration.

D is the dark charge. Figure 3 illustrates typical zero absorbance spectra for one scan. The increase in baseline noise in the 400–450 nm and 1000–1100 nm regions is due mainly to the lack of detector response in these regions and thus decreases the performance accordingly. The RMS signal-to-noise ratio for the 500–700 nm and 700–1000 nm regions are both 1500:1 in 1 scan (25 ms scan time). Signal-to-noise ratio can be increased to over 20,000:1 in 5 seconds by spectral averaging.

2.3.2. Dynamic range

To illustrate dynamic range capabilities, KMnO_4 solutions in the 1.0×10^{-6} to 5.0×10^{-3} molar concentration range were prepared and analyzed using a 1.0 cm quartz transmission cell in the visible region. Each spectrum was acquired by averaging 32 spectra with an exposure time of 30 ms/scan. Figure 4 illustrates the absorbance maximum at 525 nm vs KMnO_4 concentration. The instrument is linear to 1.3 optical densities with a correlation coefficient of 0.995 between KMnO_4 concentration and absorbance. This corresponds to a stray light figure of 0.05% and is comparable to most conventional grating based optical spectrophotometers.

Acquiring spectra of highly scattering materials can cause problems when obtaining the reference and sample spectra due to the large difference in light intensity that reaches the detector. This problem is exemplified by the SW-NIR method for determining the water/oil ratio of margarine butter using a transmission cuvette. Figure 5a shows the intensity spectra of an empty 2 cm transmission cell and one filled with margarine using a 30 ms scan rate. Because the water/oil

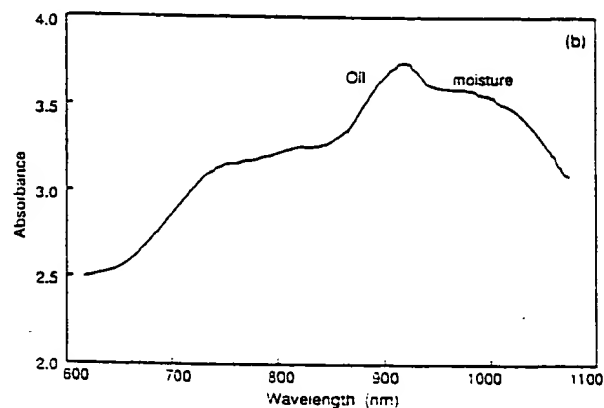
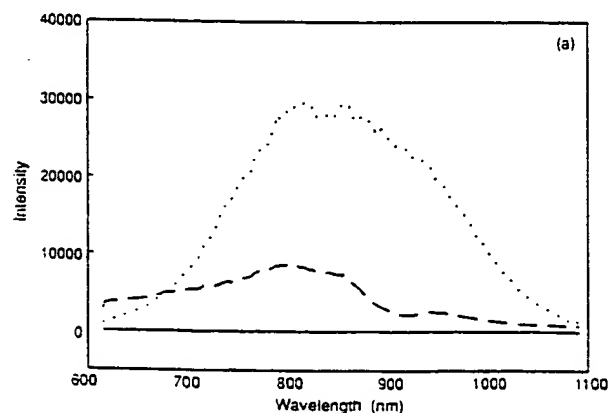


Fig. 5. (a) Intensity spectra for margarine study. (···) Reference intensity spectrum (30 ms/scan), (— — —) Margarine intensity spectrum (15 s/scan), and (—) margarine intensity spectrum (30 ms/scan). (b) Absorbance spectrum of margarine (2 cm path length).

emulsion of the margarine is highly scattering, virtually no photons reach the detector causing the margarine signal to be inundated by the detector dark charge. Charge coupled device detectors exhibit a high degree of linearity between detector photon response and exposure time [5], therefore, slower detector scan times can be utilized to collect more light before read out by the A/D circuit thus increasing the sample signal and the over all spectral signal-to-noise ratio. Using the same margarine sample as before, the exposure time was lengthened to 15 seconds/scan. The resulting margarine spectrum is shown in Fig. 5b. In order to calculate absorbance using different exposure times, the intensity spectra are normalized to the same time period after subtraction of the dark charge (with equal time exposure):

$$A = \log_{10} \left(\frac{(I_r - D_{Tr})/T_r}{(I_s - D_{Ts})/T_s} \right) \quad (2)$$

where A is the calculated absorbance, I_r is the intensity spectrum of the reference, D_{Tr} is the dark charge for the reference, T_r is the exposure time of I_r and D_{Tr} , I_s is the intensity spectrum of the sample, D_{Ts} is the dark charge for the sample, and T_s is the sample exposure time. It should be realized that this method only works if the sample uniformly scatters light over the entire spectral region as with the illustrated margarine sample and not for systems where there is a single absorbing wavelength region as with the KMnO_4 study.

2.3.3. Spectral resolution

The spectral resolution of the instrument is 10 nm at 550 nm and 16 nm at 850 nm measured by illuminating the input fiber with a narrow band of light from an external monochromator. Although the spectral resolution is quite low, the instrument does ac-

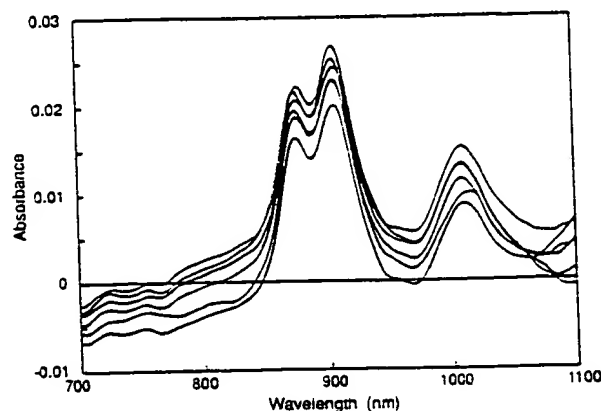


Fig. 6. Xylene mixture spectra (1 cm path length).

quire wavelength information at 0.33 nm/diode and 0.5 nm/diode in the visible and SW-NIR, respectively. This high data resolution allows the instrument to accurately determine sample constituent information even with highly overlapping spectral information. To illustrate this, a study of the three xylene isomers was made to determine whether this low spectral resolution posed a limitation [6]. Twenty-four samples were made with varying percentages of *o*-, *m*-, and *p*-xylene in the 1-95% concentration range and their spectrum acquired using a 1 cm path length cell, 30 ms scan time, and averaging 33 spectra for a total of 1 second analysis time (Fig. 6). Pure component spectra were also obtained and are illustrated in Fig. 7. Note that the aromatic C-H stretch at 860 nm for the three different isomers are highly overlapping. A second derivative transformation was calculated and the resulting derivative spectra were analyzed using a 'leave one out' cross-validation two-block partial least squares (PLS) algorithm with mean centering and two latent variables [7]. The results gave a standard error of prediction of 1.3%, 1.6%, and 1.1% for *o*-, *m*-, and *p*-xylene, respectively, which are quite good considering the non-optimized cuvette path length and data acquisition time. It should be realized that

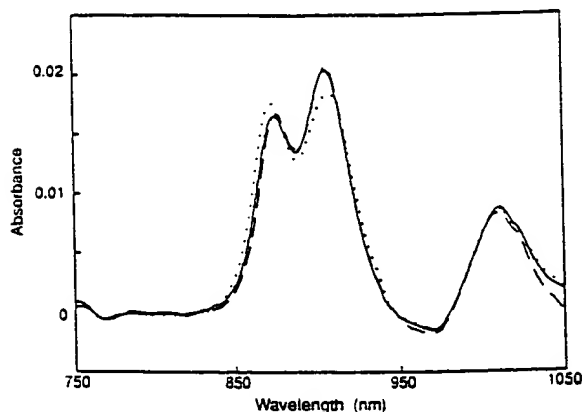


Fig. 7. Pure spectra of xylenes (1 cm path length). (···) *o*-xylene, (— — —) *p*-xylene, and (—) *m*-xylene.

these results could be greatly improved by increasing the sample path length to 4–10 cm and increasing the number of spectral averages. Clearly from these results, the instrument is capable of precise measurements without high spectral resolution.

2.3.4. Long term stability

A major factor to the success of an on-line analyzer is its ability to reproducibly acquire spectra for a long period of time without significant instrumental drift. Accordingly, the long term stability of the DPA200 was tested for absorbance and wavelength stability over a five day period. A visible instrument was setup using a single 600 μm fiber to illuminate a 1 mm thick didymium filter (Schott Glass #BG-20) and a second single 600 μm fiber optic cable was used to pick up the transmitted light and guide it back to the instrument. A reference spectrum was obtained before placing the filter in the filter holder at time zero. Spectra were then taken at 1 hour intervals for five days. The absorbance maximum of the two prominent spectral features (539 nm and 585 nm) were then calculated using a second order polynomial peak finding algorithm (DSquared Development Chemometric Toolbox). Figure 8 illustrates the drift of the 539 nm and 585 nm

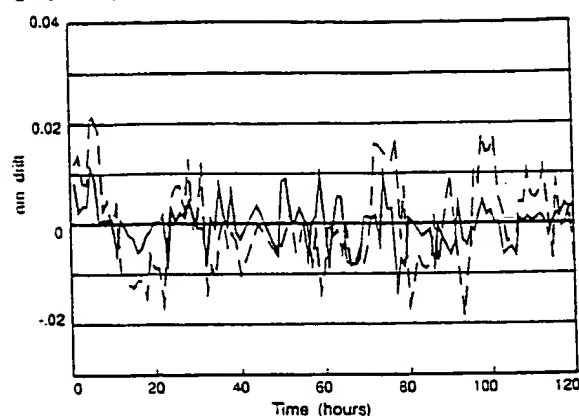


Fig. 8. Wavelength drift over time. (— — —) 535 nm peak (Std = 0.011 nm), and (—) 585 nm peak (Std = 0.0046 nm).

didymium peaks over time and shows a peak drift with a standard deviation of less than 0.011 nm and 0.0046 nm, respectively, over the five day period. Figure 9 shows the absorbance drift over the same five day period for the same didymium absorbance peaks. The standard deviation associated with absorbance drift for the 539 nm (≈ 0.25 AU) and 585 nm (≈ 0.7 AU) didymium peaks are 0.0017 and 0.0033 absorbance units, respectively. The absorbance drift at 650 nm, where there is no spectral absorbance, has a standard deviation of 0.0006 absorbance units.

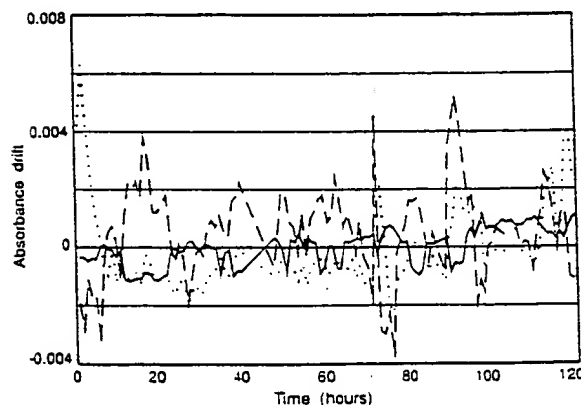


Fig. 9. Absorbance drift over time. (···) 535 nm (Std = 0.0017 abs.), (— — —) 585 nm (Std = 0.0046 abs.), and (—) 650 nm (Std = 0.0006 abs.).

3. CONCLUSION

From this discussion, the instrument presented exhibits performance features that satisfy the requirements for on-line installations. It has performance specifications equal to or exceeding those of other commercially available designs. Of particular importance is its long term stability performance.

Although the instrument has been designed for industrial applications, it can be equally used in the laboratory for routine spectroscopic analysis because of its small size and ease of operation via a host PC. In addition, the instrument has been found ideally suited for applications such as flow injection analysis (FIA) by utilizing its control capabilities. Here, a number of pumps and valves can be directly controlled by the instrument while acquiring spectral information and can lead to more repeatable FIA

analyses due to more accurate timing. Other uses include the direct control of electrochemical potentiostats and similar devices for spectro-electrochemistry experiments.

REFERENCES

- 1 D.M. Mayes and E.H. Baughman, NIR applications in process analysis, *Am. Lab.*, Oct. (1989) 54.
- 2 E.W. Ciurczak, Analytical applications of near-infrared spectroscopy *Chemtech*, June (1992) 374-380.
- 3 D.M. Mayes and J.B. Callis, A photodiode array based near-infrared spectrophotometer for the 600-1100 nm wavelength region, *Appl. Spectrosc.*, 43 (1989) 27.
- 4 J. Coates, T. Davidson and L. McDermott, The design and application of spectrometric analyzers for the chemical process industry, *Spectroscopy*, 7(9) (1992) 40.
- 5 1991 Loral Fairchild CCD Databook. Loral Fairchild, Milpitas, CA, 1991.
- 6 M.J. Lysaght, Ph.D. Dissertation, Univ. of Washington, Seattle, WA, 1991, Chap 5.
- 7 M.A. Sharif, D.L. Illman and B.R. Kowalski, *Chemometrics*. Wiley, New York, 1986.